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Characterisation of agricultural waste-derived biochars and their sorption potential for sulfamethoxazole in pasture soil: A spectroscopic investigation

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HIGHLIGHTS

- High temperature chars showed enhanced adsorptive potential, compared to low temperature chars.
- Oxygen containing acidic functional groups of biochar play negligible role in sorption.
- Biochar properties like specific surface area and aromaticity enhanced its sorption capacity.
- Amendment of pine sawdust biochar to soil significantly enhances its sulfamethoxazole sorption.

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ABSTRACT

We investigated the effects of feedstock type and pyrolysis temperatures on the sorptive potential of a model pastoral soil amended with biochars for sulfamethoxazole (SMO), using laboratory batch sorption studies. The results indicated that high temperature chars exhibited enhanced adsorptive potential, compared to low temperature chars. Pine sawdust (PSD) biochar produced at 700 °C using the steam gasification process exhibited the highest sorptive capacity (2-fold greater than the control treatment) for SMO among the three biochars used. Soils amended with green waste (GW) biochars produced at three different pyrolysis temperatures showed a small increase in SMO sorption with the increases in temperature. The NMR spectra, the elemental molar ratios (H/C, O/C) and polarity index (O + N)/C of the biochars revealed that PSD biochar possessed the highest degree of aromatic condensation compared to CC and GW chars. These results correlated well with the sorption affinity of each biochar, with effective distribution coefficient (K_d^{eff}) being highest for PSD and lowest for GW biochars. X-ray photoelectron spectroscopy results for the biochars showed a relatively large difference in oxygen containing surface functional groups amongst the GW biochars. However, they exhibited nearly identical sorption affinity to SMO, indicating negligible role of oxygen containing surface functional groups on SMO sorption. These observations provide important information on the use of biochars as engineered sorbents for environmental applications, such as reducing the bioavailability of antibiotics and/or predicting the fate of sulfonamides in biochar-amended soils.

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1. Introduction

Biochar is a biomass-derived carbonaceous material produced when any form of organic biomass (e.g. forestry, crop residue, paper mill sludge, and poultry waste) is burnt without oxygen at temperatures generally between 350 °C and 700 °C through a process known as pyrolysis (Kookana et al., 2011; Singh et al., 2010). Laboratory, field studies, and traditional farming practices suggest that deliberately added biochar can have significant impact on soil fertility, crop production, and availability of nutrients (Kookana et al., 2011; Lehmann, 2007). However because of its high specific surface area, hydrophobic nature and greater degree of aromaticity, the material has been found to be quite effective in sorbing a range of organic and inorganic compounds both in water and soil systems (Sun et al., 2011; Uchimiya et al., 2011; Wang et al., 2010; Wannapeera et al., 2011; Wu et al., 2013; Xie et al., 2014; Yao et al., 2012b; Yu et al., 2006). Biochar incorporation to soil might be an effective remediation technique for pastoral land contaminated with veterinary antibiotics and other nutrients associated with faecal and urinary excretion by grazing animals (Srinivasan et al., 2014). This would potentially help to reduce the risk that these compounds are likely to pose to the receiving environment. However,

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prior knowledge on the ability of biochar to remove contaminants of interest is essential.

The sorption affinity of biochar for pesticides such as atrazine and simazine has been shown to increase with decreasing solid/solution ratio (Zheng et al., 2010). The authors attributed this to the particle size of biochar as small particle size would mean that sorption equilibrium would be reached quickly. Teixido et al. (2011) reported unconventional adsorption behavior of the veterinary antibiotic sulfamethazine on a charcoal when investigated as a function of concentration, pH, inorganic ions, and organic ions and molecules. Several authors have examined the differences in properties of the biochars produced from different feedstocks (Lian et al., 2014; Mao et al., 2013; Yao et al., 2012a,b; Zheng et al., 2010) and at different pyrolysis temperatures (Chen and Chen, 2009; Xie et al., 2014; Zheng et al., 2013) and their influence on contaminant sorption. However, these studies were confined to investigating the sorptive capacity of biochar for aqueous systems. Only a few studies have investigated the retention ability of contaminant such as steroid hormones (Sarmah et al., 2010), pesticide (Wang et al., 2010), and phenanthrene (Zhang et al., 2010) in biochar amended soils, and none so far involving veterinary antibiotic. For example Wang et al. (2010) demonstrated that biochar obtained from high temperature pyrolysis showed significant enhancement on adsorption of herbicide terbuthylazine onto soils with an enhancing factor of 63. Similarly in another separate study biochar amendment generally enhanced the soil sorption of phenanthrene (Zhang et al., 2010). In most cases, the underlying mechanisms relating to the retention capacity of various types of biochar for organic contaminants/nutrients have not been clearly understood.

Sorption of sulfonamides on biochars is poorly understood and fundamental knowledge on how biochar reacts with various organic contaminants and with soil biological constituents is important to engineer them to meet specific environmental applications, such as remediation of contaminated land (Kookana et al., 2011). SMO antibiotic, which belongs to the sulfonamide group was used as a model compound for this study given it is widely used in the treatment of livestock in NZ, and also due to its ubiquitous occurrence in surface and groundwater. For instance, SMO was detected at a concentration of up to 0.48 μg L^{-1} in surface water samples in Germany (Hirsch et al., 1999). SMO was also detected in groundwater at a concentration of 0.22 μg L^{-1} (Lindsey et al., 2001) and in monitoring well samples (Barber et al., 2009), and streams (Kolpin et al., 2002) in the USA. These studies show that there is a possibility that these chemicals be may be encountered in drinking water supply.

The overarching objective of this study therefore was to investigate the key factors responsible for antibiotic adsorption onto biochar surface, and specifically 1) to determine the effects of feedstock type and pyrolysis temperatures on the sorptive efficacy of biochar amended model soil for SMO antibiotic, and 2) to elucidate the mechanisms involved during the sorption of SMO onto biochar amended soil using a range of spectroscopic investigations.

2. Materials and methods

2.1. Soil

Matawhero silt loam soil (0–5 cm) representative of the dairy farming region of Hawke's Bay in the North Island of New Zealand was collected, air-dried, and sieved (2 mm). A full description of the soil and the methods used to determine the physico-chemical properties can be found elsewhere (Srinivasan et al., 2014).

2.2. Biochars

Biochars used in this study were prepared from greenwaste (GW), corncob (CC) and *Pinus radiata* sawdust (PSD). The feedstock for GW biochar consisted of mixture of leaves, grass clippings, twigs and plant prunings. It was produced at a three different operating temperatures (350 °C, 450 °C and 550 °C) with a mean residence time of 20 min in a low temperature pyrolysis plant by Pacific Pyrolysis (formerly BEST Energies), Australia. CC biochar was obtained from the Hawaii Natural Energy Research Institute and was produced by a flash carbonization technique at temperature > 650 °C. PSD biochar was produced by slow pyrolysis at 700 °C and was obtained from Lakeland Steel Ltd., New Zealand.

2.3. Chemicals

SMO, (>98% purity) was obtained from Sigma Aldrich, Australia. Acetonitrile (Mallinckrodt ChromAR, ≥ 99.8% purity), and dichloromethane (Mallinckrodt UltimAR, ≥ 99.9% purity) were obtained from Thermo Fischer Scientific Ltd. New Zealand. High Performance Liquid Chromatography (HPLC) grade deionised water was obtained from an onsite Arium® 61316 high performance reverse osmosis system (Sartorius Stedim Biotech GmbH, Germany).

2.4. Biochar characterisation

The biochars were homogenized and grounded to < 2 mm for most of the analyses. The pH of the biochars measured using PHM62 standard pH meter calibrated with pH 4 and 7 buffer solutions. The electron conductivity (EC) of the biochar samples were measuring using a "In House" conductance meter with a cell constant $K = 0.69\ cm^{-1}$. The laboratory protocol, consisted of char and water (1:10) shaken for 24 h in a rotary drum shaker. Following this samples were centrifuged and the supernatant was analysed for pH and EC. The C, H, N, S, O, and ash content of the biochars (proximate analysis) were determined at the Campbell microanalytical laboratory in Dunedin (New Zealand). Exchangeable cations were determined using inductively coupled plasma mass spectrometry (ICPMS) and specific surface area (SSA) for chars was measured by Brunauer, Emmett and Teller (BET) nitrogen adsorption isotherm method. The biochars were characterized for a range of properties such as heavy metal content, surface functional groups, morphological characteristics, aromaticity and the elemental composition (including C and O species). A range of techniques such as ICPMS, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), solid state ^{13}C nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) were used for this purpose. Each technique has been described in detail and is presented in the supplementary information.

2.5. Batch sorption studies

The batch sorption protocol followed was similar to the one developed by Srinivasan et al. (2014). Duplicate samples of air-dried soils (2 g) amended with the three types of biochar (sieved to < 2 mm) at two levels (0.5% and 1.0% of soil weight) were weighed into glass centrifuge tubes (35 mL) with Teflon-lined screw caps. The centrifuge tubes containing the soil and biochar were vortexed for 30 s each to ensure homogeneity. The amount of biochar added to the soil was based on biochar application rates of 5 and 10 t ha^{-1}, assuming a bulk density of 1000 kg m^{-3}, and an incorporation depth of 10 cm in the field. A stock solution of SMO antibiotic at a concentration of 1000 mg L^{-1} was prepared in methanol, covered with aluminium foil and was stored in the dark (4 °C). By adding an appropriate amount of the stock solution separately to 5 mM $CaCl_2$ solution, six different initial aqueous solution concentrations were prepared in duplicate. Aliquots of (30 mL) of SMO with six initial concentrations (1.5, 3, 5, 7.5, 10 and 15 mg L^{-1}) prepared in background electrolyte solution of 0.005 M $CaCl_2$ were added to each tube. The tubes were wrapped in aluminium foil, placed in the dark to limit photo-degradation and shaken in an end-over-end shaker (24 h). Preliminary investigation using biochar amended

Matawhero soil had shown that 24 h was sufficient for the apparent equilibrium to take place (Srinivasan et al., 2014).

2.5.1. Extraction and HPLC analysis

For CC and GW biochar amended soils following equilibration, the tubes were centrifuged at 1750 ×*g* (10 min). After centrifugation, 1 mL of the supernatant was filtered through a 0.45 μm filter into an amber glass HPLC vial for direct HPLC-UV analysis. However, for PSD biochar amended soil which exhibited high sorption capacity, an aliquot consisting of 10 mL of the supernatant was extracted with 5 mL dichloromethane (DCM). Later 1 mL of the extracted DCM was taken into HPLC vial and was evaporated to dryness under a gentle stream of N_2. Following this the contents were reconstituted in methanol (0.5 mL) and immediately analyzed using HPLC-UV/Fluorescence detection. The detection wavelength was set to 275 nm and the limits of detection (LOD) were calculated on a signal to noise ratio of 3 to 1. LOD for SMO was 0.02 μg mL^{-1} and its limits of quantification (LOQ) was 0.013 μg mL^{-1}. The isocratic elution scheme used for separating SMO has been described earlier in detail (Srinivasan et al., 2012). The sorbed amount C_s [mg kg^{-1}] was estimated by the mass difference between the initial and final concentration as follows:

$$\boldsymbol{C_s} = (\boldsymbol{C_i} - \boldsymbol{C_w}) * \boldsymbol{V_w} / \boldsymbol{m_s}$$

where, C_i is the initial solute concentration [mg L^{-1}]; C_w [mg L^{-1}] is the equilibrium solute concentration [mg L^{-1}], V_w is the solute volume [L]; and m_s is the soil mass [kg], respectively.

2.5.2. Sorption modelling

Sorption isotherms were modelled using the Freundlich model: $C_s = K_f C_w^N$, where C_s (mg kg^{-1}) and C_w (mg L^{-1}) are the equilibrium sorbed and aqueous phase concentrations respectively, K_f (mg^{1-N} L^N kg^{-1}) is the Freundlich sorption coefficient and N (dimensionless) is the measure of sorption non-linearity ($N = 1$ represents a linear isotherm). K_f was quantified by the empirical Freundlich equation in the log transformation form: $\text{Log}\, C_s = \log K_f + N \log C_w$. In order to compare sorption across different treatments, concentration-dependent effective distribution coefficient ($K_{\text{deff}} = K_f C_w^{N-1}$) was calculated. A concentration of 0.5 mg L^{-1} was used for this purpose. Likewise, concentration-dependent organic carbon-normalized partition coefficient values (K_{oc}, mg L^{-1}) for each biochar amended soil were calculated for SMO at 0.5 mg L^{-1} using the non-linear equation $K_{oc} = K_f C_w^{N-1} / f_{oc}$, where f_{oc} is the fraction of soil organic carbon.

3. Results and discussion

3.1. Proximate and ultimate analysis of biochars

The results of the proximate and ultimate analysis of the biochars showed that the total C content increased with the highest treatment temperature (HTT), and followed an order: PSD > CC > GW with PSD biochar exhibiting C content of ~91% (Table 1). Amounts of C observed in different types of biochars are a function of multitude of factors such as the HTT, residence time, moisture content of the biomass, and most importantly, the source of biomass (Downie et al., 2009). The total N content was the highest for CC biochar (1.5%) followed by GW (0.32%) and PSD biochar (0.11%). Wood derived biochars generally tend to possess higher total C content and lower total N than chars derived from biomass originating from vegetative and forestry materials (Singh et al., 2010), and this was clearly evident in the case of PSD biochar. The molar ratios of O/C and H/C are used to measure the degree of aromaticity and maturation, which is indicative of long-term stability of the biochar (Spokas, 2010). The decreased values of O/C and H/C molar ratios of the biochars correlated well with the increasing severity of treatment temperatures implying an increased aromaticity (Table 1).

3.2. Morphological characteristics

SEM images (Fig. 1) show that all biochars (CC, PSD, GW) retain their physical form of their biomass precursor and are highly macroporous. This is particularly evident in the high resolution micrographs for CC and GW biochars. In contrast, SEM images of PSD show a material having a smooth, glassy, elongated appearance, lacking the visible porosity observed in the other two biochars. The pore formation could be attributed to escaping volatiles during high temperature decomposition. It is important to note that the pores as observed by SEM images may not necessarily contribute much to the overall specific surface area (SSA) of the material. For instance, although both the CC and GW biochars appear to be highly porous as compared with PSD biochar, the SSA of PSD biochar is actually the highest (Table 1), presumably due to the high HTT used or could be attributed to the specific pyrolysis technique. A chemical analysis of biochars obtained by SEM/EDX reveals the presence of 80–95 wt.% of C and 5–20 wt.% of O as basic elements for all biochars. Woody biochars are known to have higher total C content (Singh et al., 2010), and this was clearly evident from the C peak in EDX spectra of the PSD biochar.

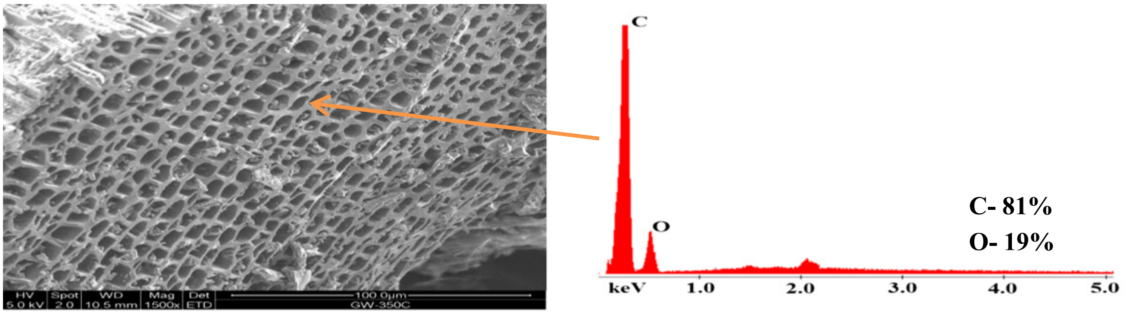
3.3. Surface functionality

The surface functional groups of the biochars were characterized using FT-IR analysis, and the FT-IR spectra for all five types of biochars and Matawhero soil are presented in Fig. 2. The spectra for PSD and CC biochar offered little information, indicating that they were fairly well aromatized. As the charring temperature raised organic groups were progressively pyrolysed to carbon, and IR absorptions for the residual organic functional groups disappeared to the extent that they became buried in the rolling baseline preventing detailed interpretation.

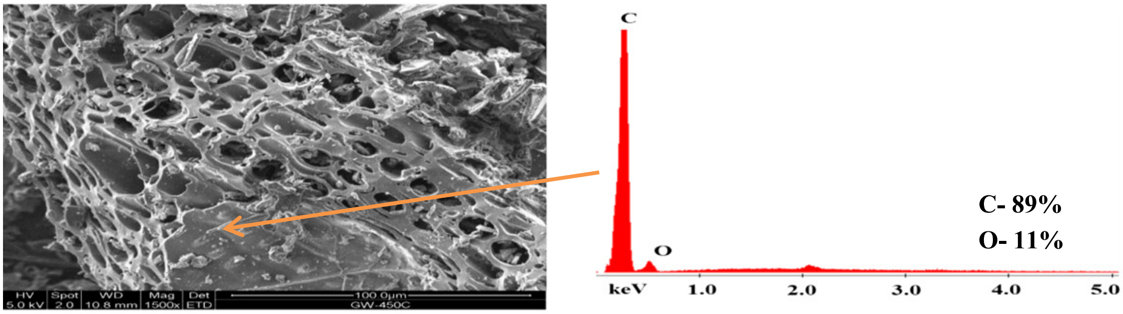
Since PSD and CC biochars were prepared at higher temperatures compared with GW biochar, their infrared spectra showed no −OH signal between 3000 and 3440 cm^{-1}. As the temperature increases the amount of water (if any) would decrease and −OH groups would be reduced via increased dehydration. The broad band observed between 3000 and 3440 cm^{-1} for GW biochars could be attributed to the presence of free and associated hydroxyl groups and structural hydroxyl groups (−COOH and −COH) of the biochar (Sitko et al., 2013). The

Table 1
Chemical properties of the biochars used in this study *specific surface area was measured by BET nitrogen adsorption; # measured by ICPMS.

Biochar/Soil	pH	Total C	Total H	Total N	Total O	O/C	H/C	(O + N)/C	EC	Exchangeable cations# cmol(+) kg^{-1}				Ash	SSA*
	(water)	(%)	(%)	(%)	(%)				(mS cm^{-1})	Ca	Mg	K	Na	(%)	(m^{2}g^{-1})
Green waste-350 °C	5.3	65.2	4.28	0.23	29.3	0.45	0.07	0.45	0.17	10.4	4.8	3.8	2.7	1.04	3
Green waste-450 °C	5.8	71.8	3.28	0.31	23.1	0.32	0.05	0.33	0.09	18.5	18.3	6.5	8.3	1.51	3
Green waste-550 °C	8.4	75.4	2.83	0.32	19.8	0.26	0.04	0.27	0.18	25.4	38.1	9.5	11.9	1.61	153
Corncob > 600 °C	9.5	82.2	2.15	1.51	8.1	0.10	0.03	0.12	4.63	2.4	15.7	123.6	1.56	6.05	186
Pine sawdust-700 °C	9.7	90.9	1.31	0.11	6.1	0.07	0.01	0.07	1.57	26.9	18.2	25.47	1.35	1.58	795
Matawhero soil	6.6	2.1	–	0.2	–	–	–	–	0.33	37.9	20.4	8.2	2.5	–	6



Green waste-350°C



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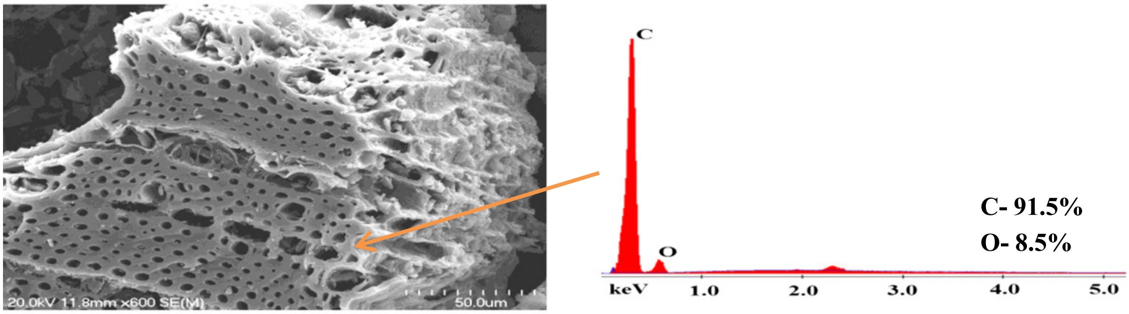
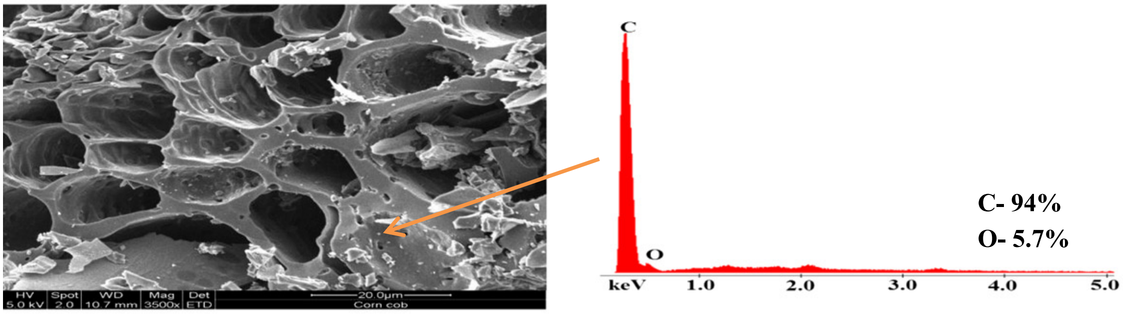
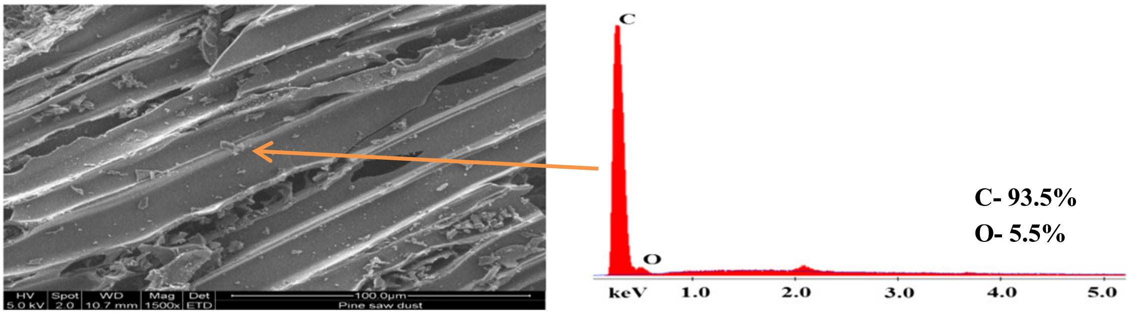


Green waste-550°C



Corn Cob



PSD

Fig. 1. Scanning electron micrographs (SEMs) of biochars along with their respective EDS spectra showing elemental wt. % of the biochar.

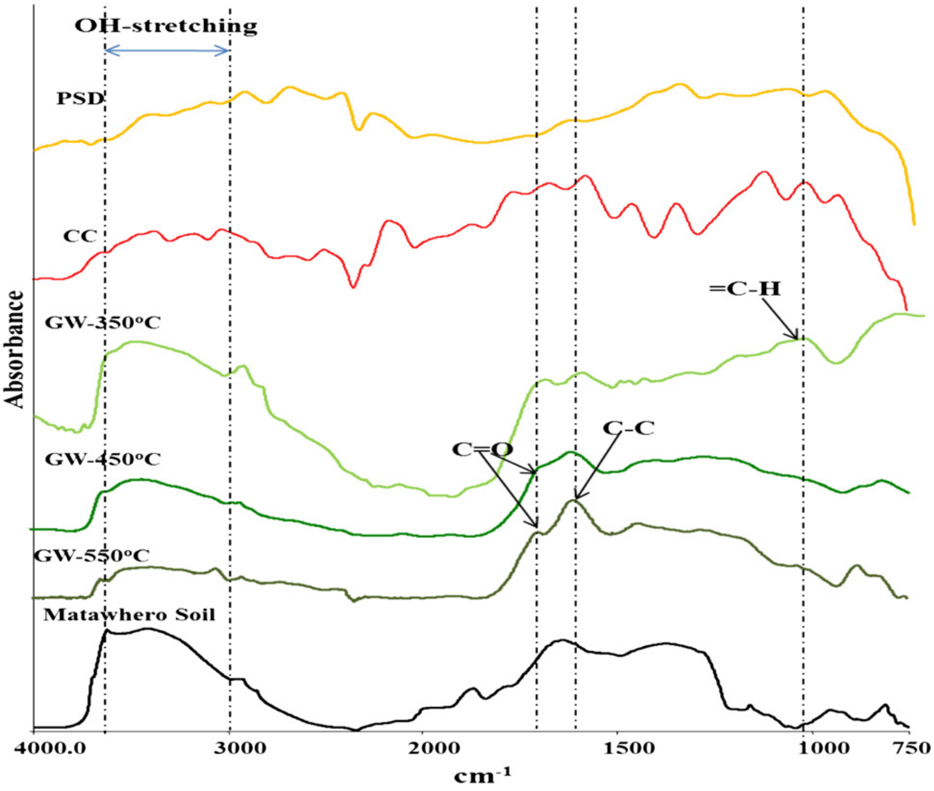


Fig. 2. FTIR spectra of the biochars along with Matawhero soil.

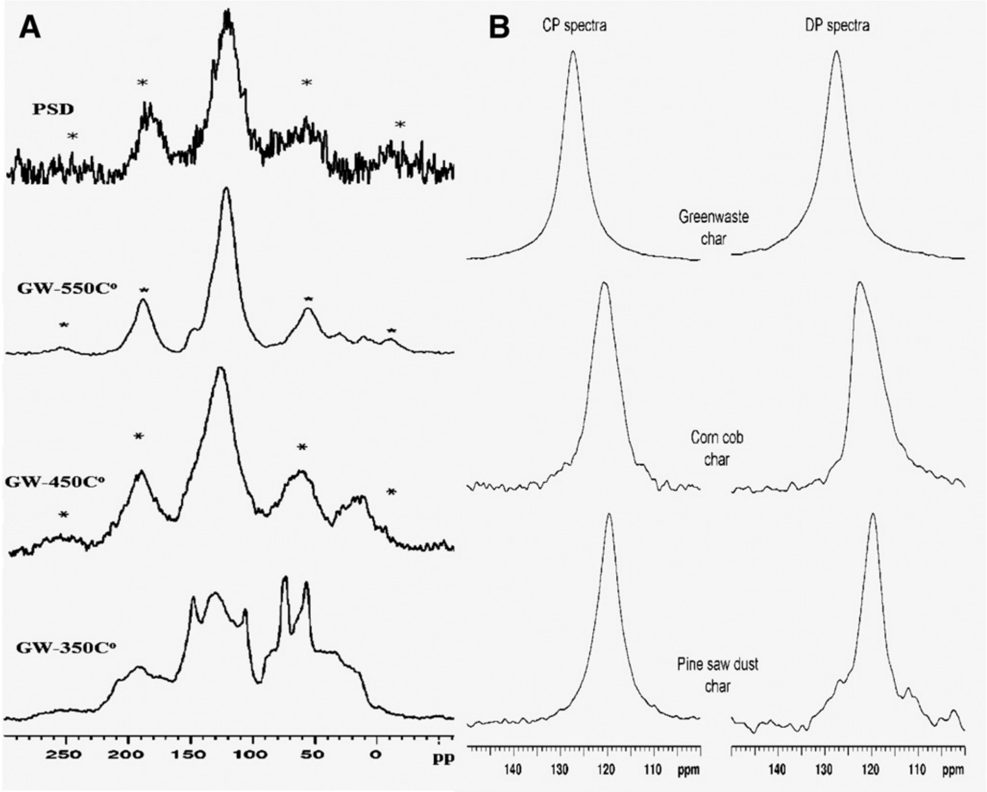


Fig. 3. (A) Solid-state ^{13}C CP NMR spectra of the PSD and GW biochars. Spinning sidebands (SSBs) associated to aromatic C are marked using an asterisk (*). (B) Solid-state ^{13}C CP and DP NMR spectra of the chars with sorbed ^{13}C-labelled benzene technique.

Table 2
NMR observabilities from spin-counting and aromatic condensation ($\Delta\delta$).

Biomass	$C_{(obs)}$ (%)	δ^{13}C-benzene-CP (ppm)	$\Delta\delta$-CP (ppm)
GW-350 °C	23.5	128.3	−0.4
GW-450 °C	8.71	127.9	−0.8
GW-550 °C	5.0	127.3	−1.4
CC-650 °C	–	–	−6.2
PSD-700 °C	3.0	119.6	−9.1

band at 1730 cm^{-1} is associated with C═O, and has been also observed in Matawhero soil. Among the GW biochars, GW-350 °C was notably different. Spectra for GW-450 °C and GW-550 °C biochars were similar with identical signals in the aromatic region.

3.4. Aromaticity

NMR spectroscopy was used to evaluate the carbon chemistry of the biochars utilizing both cross-polarisation (CP) and direct polarisation (DP) techniques. The spectra of all biochars except GW-350 °C were dominated by the aromatic C resonance centered at ~130 ppm (Fig. 3a). The spectra of biochars GW-450 °C and 350 °C do have some signal that is not due to aromatic C, a shoulder at ~150 ppm that can be assigned to O-substituted aromatic C, and two small alkyl peaks at ~15 and ~35 ppm. The spectrum of GW-350 °C is not dominated by aromatic C, although it does contain some signal in this region. The most intense peaks for GW-350 °C are in the O-alkyl region (45–110 ppm) and with a clear O-aryl peak (at 150 ppm) and alkyl signal (0–45 ppm). Table 2 shows the NMR observabilities (C_{obs}) from spin counting and aromatic condensation ($\Delta\delta$) values for the biochars used in this study. In general NMR observabilities for the biochars were very low, albeit for GW-350 °C biochar. For high temperature chars, low NMR observability is usually a consequence of conductivity and this was evident for or both CC and PSD biochars. While no spectra could be obtained for CC biochar, CP spectra for PSD showed only 3% NMR observability (i.e. 97% of potential signal was not detected), making the interpretation difficult. However, 5–24% observability was observed for GW biochars. (Fig. 3A).

The ring-current technique used to measure the degree of condensation of aromatic structures in the biochars revealed that the GW biochars had the least negative chemical shift ($\Delta\delta$), an indication of the least condensed aromatic structures associated with biochars. GW-350 °C biochar displayed a least negative $\Delta\delta$ value (−0.4 ppm) indicating the lowest degree of aromatic condensation. The CC biochar had a more negative $\Delta\delta$ (−6.2 ppm), consistent with a much higher production temperature (>600 °C). PSD biochar had an even more negative ($\Delta\delta = -9.1$), indicating a higher degree of aromatic condensation than for wood heated at 850 °C for 2 h ($\Delta\delta = -8.1$), but not quite as condensed as for commercial activated charcoal with $\Delta\delta = -10.0$ (McBeath and Smernik, 2009). Among the biochars studied, $\Delta\delta$ values suggest increasing aromatic condensation in the order GW-350 °C < GW-450 °C < GW-550 °C ≪ PSD. The $\Delta\delta$ values were consistent with expectations, when compared to $\Delta\delta$ for the thermo sequence chars of McBeath et al. (2011). Aromaticity was slightly higher and observability much higher when DP was used. DP NMR spectra of the chars with sorbed ^{13}C-labelled benzene resulted in the entire signal in these spectra being from the sorbed benzene (Fig. 3B).

Table 3
Chemical composition (at ± 1%) of the biochar surfaces as determined by XPS (wide scan).

	C	O	N	Si
GW-350 °C	81.46	18.36	–	0.17
GW-450 °C	84.56	15.12	–	0.23
GW-550 °C	90.60	9.31	–	0.09
CC	93.16	6.36	0.48	0.09
PSD	96.26	3.72	–	0.09

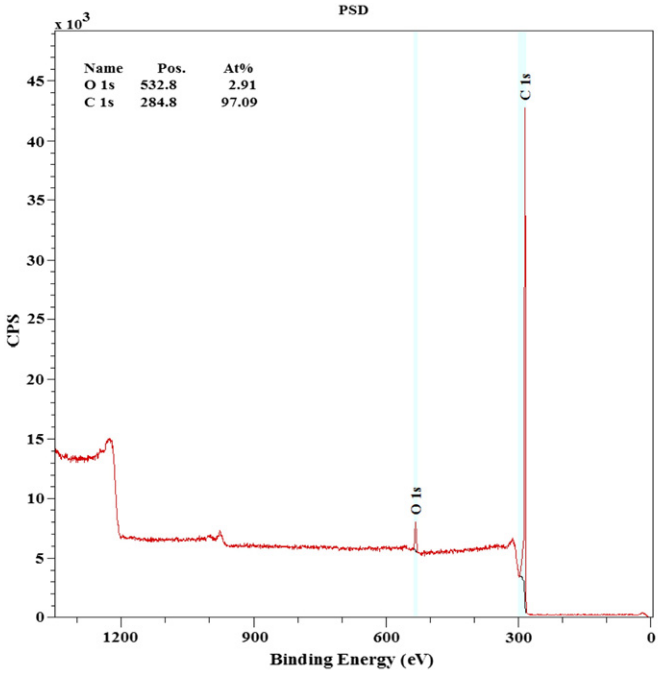


Fig. 4. Example XPS wide scan spectra for PSD biochar.

3.5. XPS analysis

The chemical composition of the biochar surfaces as determined by XPS wide scan are summarised in Table 3, with an example of wide scan spectra shown for PSD biochar (Fig. 4). Low pyrolysis temperature resulted in low C content (81.46 to 96.26%) of the biochars correlating well with results from EDX and NMR. The C 1 s and O 1 s bonding state and its relative percentage on the biochar surface are shown in Table 4 with peak deconvolution for the C1s and O1s region scan in Fig. 5. The XPS spectrum of the C1s peaks measured at increased resolution shows the main peak at 284.8 eV due to the aromatic carbon C–C and other peaks associated with oxygen containing functional groups: C–O in carbonyl (at 285.7 eV) and O–C═O in carboxylic and/or ester groups (at 289.2 eV) (Sitko et al., 2013). C 1 s spectrum for all biochars showed the presence of C═O functional groups, which are typical of lignin and carbohydrate derived biochars. Only GW-450 °C and GW-350 °C chars showed the presence O–C═O components. The XPS spectrum of O1s was deconvoluted into three peaks: the first peak with a binding energy of 533.4 eV is associated with O–C, carbonyl oxygen atoms in carboxylic groups, and ester was found in all the biochars. The second one with a binding energy of 531.9 eV can be assigned to O═C and was observed in GW-450 °C and GW-350 °C biochars, while the third one (at binding energy of ~535 eV) can be assigned to –OH functional group observed in GW-350 °C biochar only (Zhang et al., 2012). The results obtained from quantitative XPS analysis (Table 5) are in agreement with the SEM/EDS results.

Table 4
C 1 s and O 1 s bonding state and its relative atomic percentage on biochar surfaces as determined by XPS.

Binding Energy (eV)	Structure	GW-350 °C	GW-450 °C	GW-550 °C	CC	PSD
284.8	C–C	49.8	43.4	78.6	68.2	62.4
~286.0	C–O	26.0	51.9	21.4	31.8	37.6
~288.0	COOH	24.2	4.7	–	–	–
~531.5–532	C–O	26.8	10.7	–	–	–
~533	C═O	53.4	89.3	100	100	100
~535	–OH	19.8	–	–	–	–

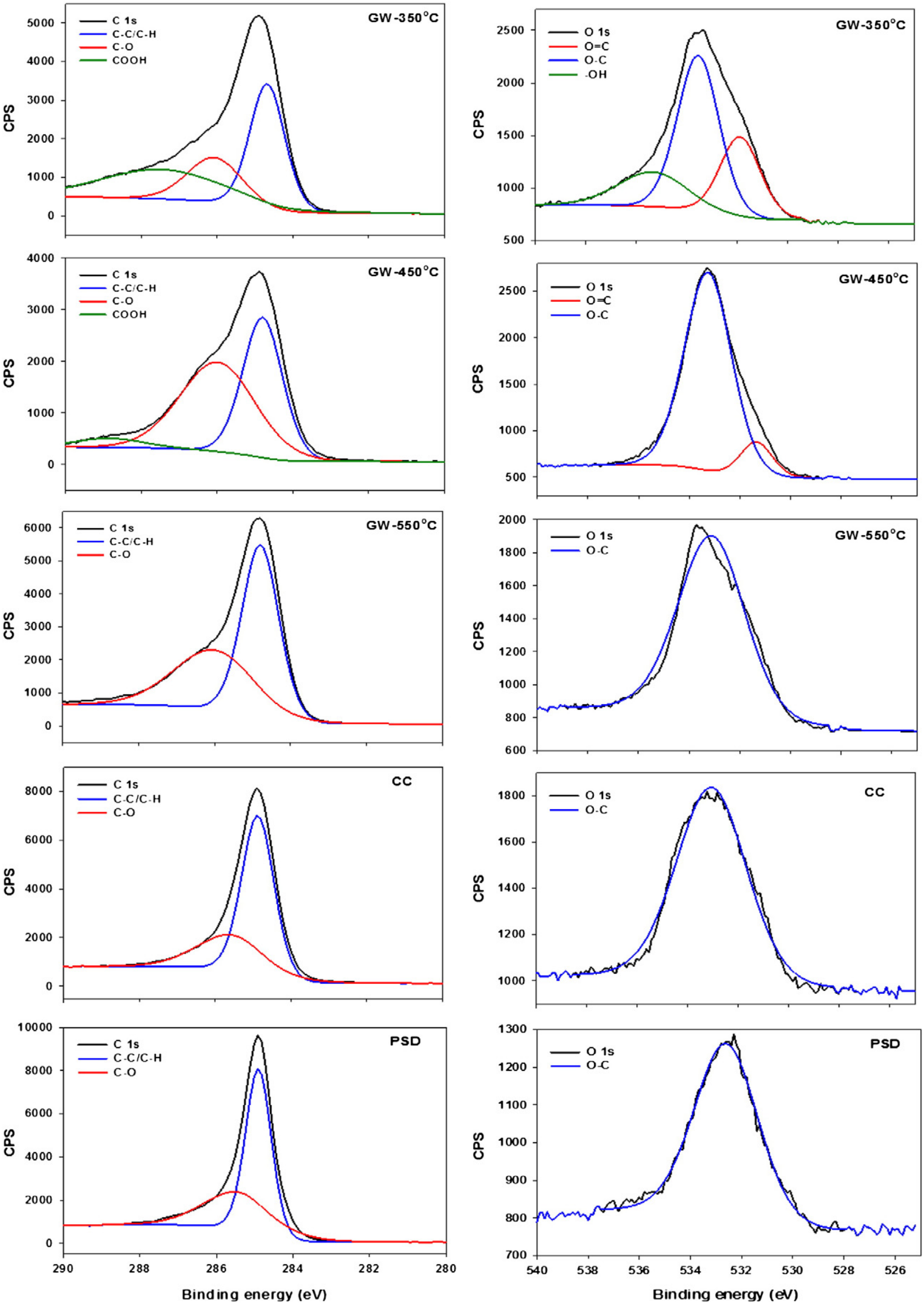


Fig. 5. C1s and O1s region scan of the biochars along with its peak deconvolution.

Table 5
Summary of sorption parameters for SMO antibiotic derived from the multiple-concentration isotherms in Matawhero soil amended with biochars.$^{\#}K_d^{eff}$ is the concentration dependent effective sorption distribution coefficient.

Treatment	K_d	R^2	K_f	N	R^2	K_d^{eff}	Log K_{oc}*
0.5% GW-550 °C BC + soil	1.55	0.64	2.86	0.72	1.00	2.56	2.09
0.5% CC BC + soil	3.47	0.82	8.55	0.55	0.93	7.11	2.53
0.5% PSD BC + soil	13.89	0.94	28.51	0.61	0.88	24.34	3.06
1.0% GW-550 °C BC + soil	1.63	0.95	2.74	0.76	0.99	2.48	2.07
1.0% GW-450 °C + soil	1.53	0.93	2.70	0.78	1.00	1.99	1.98
1.0% GW-350 °C + soil	1.31	0.94	2.18	0.75	0.98	2.44	2.07
1.0% CC BC + soil	5.29	0.74	11.89	0.61	0.96	10.16	2.68
1.0% PSD BC + soil	33.7	0.65	66.99	0.45	0.96	53.53	3.41
Soil without BC	1.40	0.90	2.37	0.75	1.00	2.83	2.13

($K_d^{eff} = K_f\ C_w^{N-1}$) using lowest aqueous equilibrium solution concentrations of $C_w = 0.5$ mg L^1; *concentration dependent OC-normalized sorption coefficient calculated using $K_{oc} = K_f\ C_w^{N-1} foc^{-1}$ at $C_w = 0.5^*$ mg L^{-1}; K_d^{eff} in L kg^{-1} and K_f in mg $^{1-N}$ L ^{N} kg^{-1}.

3.6. Batch sorption studies

Sorption isotherms for SMO in the three different biochar amended soils along with their Freundlich model fits are shown in Fig. 6. Except for GW amended soil, all isotherms were found to be highly nonlinear with N values ranging from 0.55 to 0.72 and 0.45 to 0.76 at application rate of 0.5% and 1% of soil wt. respectively (Table 5). However, the amount of biochar (0.5% and 1.0%) added to the soil did not have a marked effect on the overall sorption non-linearity. The effective distribution coefficient (K_d^{eff}) values for SMO at the lowest equilibrium concentration ($C_w = 0.5$ mg L^{-1}) ranged from 2.48 to 53.5 L kg^{-1} in biochar amended soils. There was no marked difference in K_d^{eff} values for SMO between soils treated with 0.5% and 1% CC and GW biochar respectively with corresponding log K_{oc} values in soil amended with GW, CC and PSD biochars were similar (2.53–2.68) for the two treatments. In contrast, large differences with respect to the antibiotic sorbed and amount of biochar added were found for the soil treated with 0.5% and 1% PSD biochar.

The soil amended with 1% PSD biochar showed a 20-fold increase in sorption affinity for SMO as compared with the control treatment; however, increase in antibiotic uptake by the soil amended with 1% CC was only 4-fold. Adding 1% GW biochar to soil did not improve SMO sorption, and surprisingly, the control, and 1% GW biochar amended soil rather showed similar K_d^{eff} values (2.48 and 2.56 L kg^{-1}). Addition of 0.5% of PSD biochar caused an order of magnitude increase in K_d^{eff} for SMO, while at double the amount of biochar in the soil, uptake of SMO was increased by 20-fold (Table 5). A recent study on wood derived biochar showed K_d values for SMO to range from as low as 2 to 104 L kg^{-1} (Yao et al., 2012b); however, this study did not involve any soil amendments, and experiments were performed in aqueous solution with biochar.

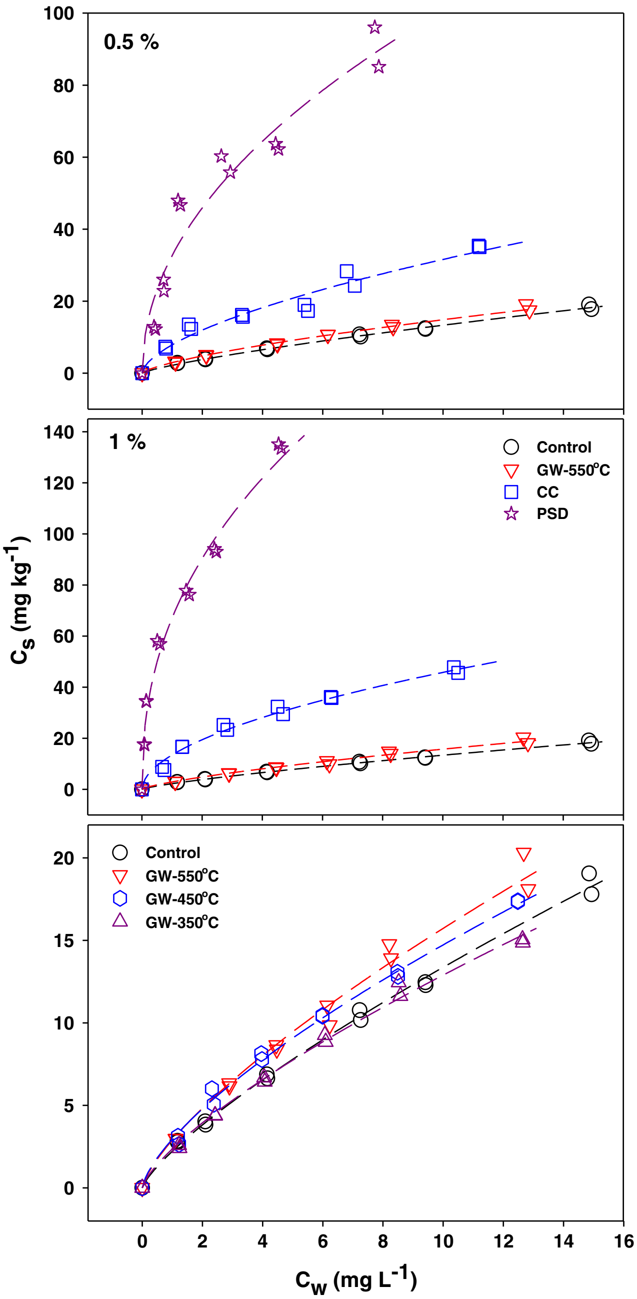


Fig. 6. Multiple-concentration batch sorption isotherms (24 h contact) for SMO during its equilibration with soil amended with 3 types of biochar at 0.5% (top plot), and 1% (middle plot) by soil weight along with 3 types of GW biochar at 1% by soil weight (bottom plot). Symbols represent measured values while solid lines represent Freundlich model fits.

3.6.1. Influence of biochar feedstock and SSA on sorption

All biochars were produced from different feedstocks, using different techniques, and under different conditions and as a result the physicochemical properties of the biochars varied considerably (Table 1). The enhanced SMO sorption in PSD biochar amended soil as compared to other biochars could be attributed to high SSA (795 $m^2 g^{-1}$) which is comparable to commercially available activated carbon (~1000 m^2 g^{-1}). Similar findings were also reported for phenanthrene and SMO sorption with high pyrolysis temperature (Wu et al., 2013), and for corn straw derived biochar sorption for soil fumigant, 1,3-dichloropropane (Graber et al., 2011).

Low SMO sorption affinity of soil amended with GW biochar can be also linked to the exchangeable cations present in the biochars (Table 1). The presence of cations as salts, and in higher amounts has been linked to the increases in the hydrophilic nature of the char, hindering sorption of organic contaminants on to its surface in an earlier study (Bornemann et al., 2007). In our work, the sum of the exchangeable cations in the CC biochar was the highest (~140 cmol (+) kg^{-1}) among the three biochars, followed closely by GW and PSD biochars. Among all treatments, soil amended with PSD biochar gave the highest log K_{oc} values. The result was consistent with the higher SSA and lower sum of total cations present in the PSD biochar compared to other chars. However, for CC biochar despite having higher values for the total exchangeable cations compared to PSD, its sorption affinity for the antibiotic in amended soil was markedly lower than PSD biochar amended soil. This could be presumably due to the much lower surface area and carbon content in the CC biochar.

3.6.2. Effect of pyrolysis temperature on sorption

Given there was no marked difference between the K_d^{eff} values for SMO in soils treated with 0.5% and 1% GW-550 °C biochar, we used only one application rate (1% by soil weight) and investigated the pyrolysis temperature effect on sorption. Fig. 6 displays the sorption isotherms for SMO in soil amended with the three GW biochars produced at three temperatures along with the Freundlich model fits. Overall K_f values for SMO in GW amended biochars slightly increased with the increase in temperature. However, sorption values would suggest that increase was minimal, and unlikely to be statistically significant, though a linear trend was obvious from the data in Table 5. Addition of biochar to the soil enhanced the linearity of the isotherms compared with the control, which was highly non-linear ($N = 0.33$). This was contrary to the findings of Chen and Chen (2009), where the authors reported a progressive change in sorption isotherms leaning from linear to Freundlich type with the increasing temperatures. The nonlinearity of sorption isotherms is a characteristic of sorption processes arising from site-specific interactions occurring on the carbonized phase of the biochar. These types of non-linear behaviour for hydrophobic contaminants could be attributed to the broad range of interaction energies, as well as to the high degree of variability in those energies from one sorbent to another (Weber et al., 1992).

The low adsorption capacity of GW biochars in biochar/soil mixtures could be attributed to the presence of acidic surface functional groups that could hinder the ability of biochar to adsorb organic contaminants (Tessmer et al., 1997). Another plausible explanation could be the masking effect of one adsorptive phase (soil) over another adsorptive phase (biochar) such that the total surface area available for sorption is reduced. Zheng et al. (2013) investigated the sorption of all species of SMO onto biochars produced at 300–600 °C, and observed good correlation between the sorption and temperature increment. It is to be noted that in our study, pyrolysis temperature did not have a marked influence on the sorptive capacity for SMO as a single species, while Zheng et al. (2013) investigated the sorption of all the species of SMO. This could be a plausible explanation for the disparity between the present study and earlier work of Zheng et al. (2013). Elsewhere, biochar produced for orange peel at 700 °C displayed the maximal sorption capacity for naphthalene and 1-naphthol compared to the chars produced at lower temperature in biochar-aqueous system (Chen and Chen, 2009). Given the differences of the two systems (biochar-soil and biochar-aqueous) used in these studies, a direct comparison may be inappropriate as multitude of factors could potentially influence the overall sorption process. When HTT was increased from 350 °C to 450 °C, there was no change in the SSA value (very low at 3 $m^2 g^{-1}$), but upon further increases in the temperature (550 °C) there was a sudden rise in the SSA (153 $m^2 g^{-1}$). Similarly Yao et al. (2012b) reported significant differences in the SSA for 4 biochars prepared at low temperature (450 °C) and high temperature (600 °C). Since 550 °C was the highest HTT investigated in our study, it is difficult to conclude whether it is the optimum temperature for GW biochar.

3.6.3. Effect of aromaticity and surface functional groups on sorption

Results from Table 1 show that H/C ratios for PSD and CC char were very low, which means that these chars have very highly condensed aromatic ring system (Knicker et al., 2005). For the GW biochars, the molar ratios (H/C and O/C) also decreased with increasing pyrolysis temperature. NMR results reveal that GW-550 °C was more aromatic as compared to 450 °C and 350 °C. As a result of increasing pyrolysis temperatures from 350 to 550 °C, the values of the polarity index, $(O + N)/C$ for GW biochars also decreased (Table 1), and subsequent reduction of the polar functional groups due to increased pyrolysis temperature. This was substantiated through a plot (not shown) of polarity index $(O + N)/C$, atomic ratios H/C and O/C against the pyrolytic temperatures and resulted in a strong negative correlation (R^2 range of 0.95–0.98). Disappearance of polar functional groups ($-OH$, COOH, $C-O$) with increased temperature was evident in both the FTIR and XPS spectra. These observations suggest the role of aromaticity in sorptive potential of the high temperature biochars for SMO in amended soils.

The NMR and the elemental ratios results indicated that PSD biochar showed the highest degree of aromatic condensation compared to CC and GW chars. These results correlated well with the sorption affinity of each biochar, i.e. K_d^{eff} being highest for PSD and lowest for GW biochars. Ji et al. (2011) showed that adsorbent surface area-normalized adsorption of SMO to be higher on the demineralized black carbon than on nonporous graphite due to the micropore-filling effect. The authors estimated the contribution of black carbon to the overall sorption to bulk soil was significant and important for SMO antibiotic. Similarly in a more recent study, the adsorbent surface area-normalized adsorption for two sulfonamides was stronger to biochar (pine-wood) produced at 500 °C than 400 °C. This was attributed to the enhanced π–π electron-donor–acceptor interaction with the carbon surface of C500 due to the higher degree of graphitization (Xie et al., 2014).

The presence of surface functional groups in biochar is responsible for a range of processes that take place during the biochar-soil interactions. Biochar with carboxylic acid ($-COOH$) groups, when mixed with soil can improve the cation exchange capacity of soil, which could intern effect the sorption capacity of soils for organic compounds (Wu et al., 2013); and control heavy metal sequestration ability in soils (Uchimiya et al., 2011). The XPS C 1 s spectra confirmed the presence of $C-C$ and $C{=}O$ functional groups in all biochars. However, their percentage components varied among the biochars. Among the three different biomasses used, GW-550 °C biochar had the highest C–C (78.6%) component compared to CC (68.2%) while being lowest for PSD (62.4%). On the contrary $C{=}O$ component was highest for PSD (37.6%) and lowest for GW-550 °C (21.4%). These findings lend further support to our argument that $C{=}O$ component of biochar could play an important role in enhancing the sorption affinity of PSD biochar. However, among the GW biochars $C-C/C-H$ component increased, while $C-O$ decreased with the increases in the pyrolytic temperature. GW biochars at lower pyrolysis temperature (350–450 °C) showed the presence of $O-C{=}O$ peaks in the XPS spectra. For GW biochars none of C 1 s component influenced its sorption affinity to SMO antibiotic, lending further support to our argument that the surface functional groups of the biochar did not have any influence on the antibiotic sorption affinity.

Recently Xie et al. (2014) produced two sets biochars of from pinewood at 500 °C, one of the 500 °C biochar was hydrogenated following pyrolysis. The authors reported that despite having the relatively large difference in surface O-functionality content, the two biochars exhibited nearly identical adsorbent surface area-normalized adsorption, indicating negligible role of surface O-functionalities on the sorption mechanisms to the biochars derived from pine wood. In an earlier study the presence of acidic surface functional groups was shown to hinder the ability of activated carbon to adsorb phenolic compounds under oxic conditions by reducing its effectiveness in promoting adsorption via oxidative coupling reactions (Tessmer et al., 1997). However, in contrary to our findings, biochar (B250) prepared at 250 °C exhibited 2–7 times higher sorption capacity to SMO than those prepared at higher temperatures (800 °C) (Lian et al., 2014). The authors attributed the high sorption capacity of B250 to the negative charge-assisted H-bond and due to its abundant O-containing groups. A plausible explanation could be that the sorption affinity of the biochar could be an intrinsic property of its original feedstock, operating temperature and residence time which were different in these studies.

4. Conclusions

We have demonstrated that readily available agricultural biomasses such as corncob, green waste and pine sawdust hold promise as a effective adsorbent for the uptake of antibiotic residues and other contaminants associated with land-application of effluents. However, controlling the production technique is necessary to ensure that the biochar has the required characteristics for contaminant sequestration. SMO removal efficiency for GW, CC and PSD were 2.7, 17.9 and 50.3% at 0.5% (wt.) biochar addition and 2.7, 25.8, 72.9% at 1% biochar addition. The addition of biochars made from PSD and CC to soil resulted in increased SMO uptake in the model soil suggesting decreased mobility potential for SMO in the pastoral region. Increasing the antibiotic fixation to soils should also reduce toxicity and availability to soil organisms (microbes, invertebrates and plants). PSD biochar amended soil absorbed 30 times more contaminants than soil alone which was attributed to very high SSA of the PSD biochar (four times higher than that of other biochars) and its degree of aromaticity. GW biochars produced at different pyrolysis temperatures when amended with soil, had little effect on SMO sorption. These observations provide important information on the use of biochars as engineered sorbents for environmental applications, such as reducing the bioavailability of antibiotics and/or predicting the fate of sulfonamides in biochar-amended soils.

It is conceivable that given the similarity in the functional groups within sulfonamide group, similar results to what we have observed for SMO can be expected for other antibiotics within this group. However, this may not hold true for other antibiotics of different groups (e.g. macrolide, tetracycline, fluoroquinolones), and much work is required to investigate this aspect. Extending the work to other NZ dairy farming soils along with investigating the desorption behaviour of biochar amended soils could be a focus for future research.

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Appendix A. Supplementary data

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